Bereiding en eigenschappen van 1-alkylthio-1-alkynen

Boonstra, Harm Jacob

SUMMARY

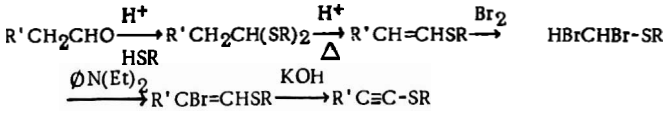
Chapter I

Preparation of 1-alkylthio-1-alkynes from aldehydes.

Thioacetals of aldehydes can be converted by pyrolysis in the presence of an acid catalyst into thioenolethers:

$$R'-CH_2-CH(SR)_2 \xrightarrow[\Delta]{H^+} R'CH=CH-SR + HSR$$

Using this reaction 1-alkylthio-1-alkynes can be prepared from the corresponding aldehydes by the following sequence of reactions:



Chapter II

(Alkylthio)ethynyl derivatives from dichloroethylene.

Cis-1, 2-bis-(alkylthio)ethenes can be prepared from *cis*-dichloroethylene or vinylidene chloride and sodium alkanethiolate in liquid ammonia (table 1):

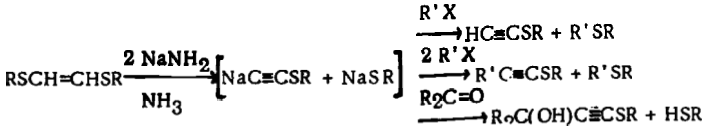
$$C_2H_2Cl_2 + 2\ NaSR \xrightarrow[NH_3]{} cis\ RSCH=CHSR + 2\ NaCl$$

The mechanisms of these reactions are discussed.

Trans-dichloroethylene or a mixture of *cis*- and *trans*-isomers can be used as a starting material, if it is first dehydrochlorinated by sodamide:

$$trans\ CHCl=CHCl \xrightarrow[NH_3]{2NaNH_2} \left[NaC\equiv CCl\right] \xrightarrow[NH_3]{2\ HSR} cis\ RSCH=CHSR$$

The *cis*-1, 2-bis-(alkylthio)ethylenes obtained in this manner can be used for the preparation of (alkylthio)ethynyl derivatives by allowing them to react with sodamide in liquid ammonia and an alkylhalide or a carbonyl compound respectively (tables 2, 3 and 4):



The 1-alkylthio-1-alkynes can be prepared in *one step* starting from dichloroethylene without isolating the intermediate *cis*-1, 2-bis-(alkylthio)ethylene (table 5):

$$CHCl{=}CHCl \xrightarrow[NH_3]{2\ NaSR} \left[RSCH{=}CHSR\right] \xrightarrow[NH_3]{2\ NaNH_2\ ;\ 2\ R'X} R'C{\equiv}CSR$$

For the (alkylthio)ethynes $RSC{\equiv}CH$ and the (alkylthio)ethynylcarbinols $R_2C(OH)C{\equiv}CSR$ this shorter method is less satisfactory.

The (alkylthio)ethynes $RSC{\equiv}CH$ however can be prepared in one step by a somewhat modified procedure from *trans*-dichloroethylene or a mixture of isomers.

$$CHCl{=}CHCl \xrightarrow[NH_3]{2\ NaNH_2} \left[NaC{\equiv}CCl\right] \xrightarrow[NH_3]{HSR} HC{\equiv}CSR$$

Chapter III

Properties of 1-alkylthio-1-alkynes.

Attention is drawn to the fact, that acetylenic compounds X-C≡C-Alkyl have a consistently higher boilingpoint than the isomeric compounds X'-C≡C-H(X and X' are alkyl or alkylthio). The difference amounts to approximately 20° and is correlated with a higher heat of evaporation and a higher polarisability of the first mentioned compounds.

In *electrophilic additions* to 1-alkylthio-1-alkynes the electrophilic fragment invariably attaches itself to C-atom 2 of the triple bond, e.g.:

$$R'C{\equiv}C\text{-}SC_2H_5 \begin{cases} \xrightarrow{H^{\oplus};H_2O} R'CH_2COSC_2H_5\ (R' = H,\ CH_3) \\ \xrightarrow[HCl]{} R'CH{=}CClSC_2H_5\ (R' = H) \\ \xrightarrow{(CH_3)_2C{=}O;BF_3} (CH_3)_2C{=}CR\text{-}COSC_2H_5\ (R' = H,\ CH_3) \end{cases}$$

In *nucleophilic additions* the nucleophilic fragment also attacks C-atom 2:

$$\underset{2\ \ 1}{CH_3\text{-}C{\equiv}C\text{-}SC_2H_5} \begin{cases} \xrightarrow{EtO^{\ominus}} CH_3C(OC_2H_5){=}CH\text{-}SC \\ \text{piperidine}\quad CH_3C(NC_5H_{10}){=}CH\text{-}SC_2H_5 \end{cases}$$

1-Ethylthio-1-propyne apparently shows the same dualism as (ethylthio)ethyne and (ethylthio)ethynecarbonic esters. The explanation is sought in a -E effect of the sulfur atom, which manifests itself only on approach of a nucleophilic agent.

The *radical-addition* of ethanethiol to 1-ethylthio-1-propyne leads to 1, 2-bis-(ethylthio)-1-propene $CH_3C(SC_2H_5){=}CH\text{-}SC_2H_5$

(Ethylthio)ethyne and (isopropylthio)ethyne easily form cristalline mercury salts:

$$R\text{-}S\text{-}C{\equiv}C\text{-}H \xrightarrow{K_2HgI_4,\ KOH} (RSC{\equiv}C\text{-})_2Hg$$

(Ethylthio)ethyne easily undergoes a *Mannich reaction:*

$$C_2H_5SC{\equiv}C\text{-}H + (CH_2O)_x + (C_2H_5)_2NH \longrightarrow C_2H_5SC{\equiv}C\text{-}CH_2N(C_2H_5)_2$$

Upon heating at 90-100° (ethylthio)ethyne decomposes and forms 2-(ethylthio)thiophene:

$$2\ C_2H_5SC{\equiv}CH \longrightarrow \underset{HC}{\overset{HC}{\diagdown S \diagup}}\!\!=\!\!\underset{C\text{-}SC_2H_5}{\overset{CH}{\diagup}} + C_2H_4$$

(t. Butylthio)ethyne behaves similary.

Chapter IV

Infrared-absorption spectra of alkylthio-compounds.

Upon studying the spectra of several, mainly unsaturated alkylthio-compounds the following conclusions could be drawn:
a) Alkylthio groups are characterised by certain distinctive absorption bands (table 1).
b) Alkylthio groups and chlorine atoms appear to exhibit considerable similarity with regard to their influence upon absorption spectra. This is especially the case for the compounds CHX= CHY (X and Y are Cl or RS). This opens the possibility of distinguishing between *cis*- and *trans*-isomers with considerable certainty. In general the elucidation of structures and a more or less thorough interpretation of absorption spectra is facilitated by this phenomenon (tables 4 and 5, figs 9 and 10).
c) Conjugation of an alkylthio group with a C= C or a C≡ C bond causes a shift of the C C stretching vibration to lower wave numbers (30-60 cm^{-1}). Conjugation of 2 or 3 alkylthio groups with a C= C bond causes even bigger shifts (60-110 cm^{-1}).
d) Alkylthio groups have the tendency to suppress the appearance of H-C= stretching vibrations.
e) In compounds of the type -C= C-SR the = C-S stretching vibration lies between 830 and 710 cm^{-1}; the frequency is very sensitive to substituents on the C= C bond and not very sensitive to variations in R.
f) In 1-alkylthio-1-alkynes RSC≡CR' the intensity of the C≡C stretching vibration is vanishingly small.

From the intensity of the C≡C stretching vibration in compounds A-C≡C-B qualitative conclusions about the magnitude of the static polar effects of the groups A and B can be drawn.